



ADVANCED INORGANIC CHEMISTRY

A Comprehensive Text

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CHAPTER TWENTY-ONE

The Elements of the First Transition Series

GENERAL REMARKS

We discuss in this chapter the elements of the first transition series, titanium through copper. There are two main reasons for considering these elements apart from their heavier congeners of the second and third transition series: (1) In each group (e.g., V, Nb, Ta) the first-series element always differs appreciably from the heavier elements, and comparisons are of limited use; and (2) the aqueous chemistry of the first-series elements is much simpler, and the use of ligand field theory in explaining both the spectra and magnetic properties of compounds has been far more extensive. The ionization enthalpies for the first-series atoms are listed in Appendix 2. The separate Sections 21-A through 21-H summarize the oxidation states and stereochemistries for each element; we do not specify, except in cases of special interest, distortions from perfect geometries that can be expected in octahedral d^1 and d^2 (slight), high-spin octahedral d^4 (two long coaxial bonds), low-spin octahedral d^4 (slight), high-spin octahedral d^6 , d^7 (slight), or low-spin octahedral d^7 , d^8 molecules (two long coaxial bonds). A few other general features of the elements can be mentioned here.

The energies of the $3d$ and $4s$ orbitals in the neutral atoms are quite similar, and their configurations are $3d^n4s^2$ except for Cr, $3d^54s^1$, and Cu, $3d^{10}4s^1$, which are attributable to the stabilities of the half-filled and the filled d shells, respectively. Since the d orbitals become stabilized relative to the s orbital when the atoms are charged, the predominant oxidation states in ionic compounds and complexes of non- π -bonding ligands are II or greater. Owing to its electronic structure, copper has a higher second ionization enthalpy than the other elements and the Cu^{I} state is important. The high values of third ionization enthalpies also indicate why it is difficult to obtain oxidation states for nickel and copper greater than II. Although ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is a very complex one and not amenable to ready gen-

22-F. RUTHENIUM AND OSMIUM¹

22-F-1. General Remarks: Stereochemistry

The chemistry of ruthenium and osmium bears little resemblance to that of iron except in compounds such as sulfides or phosphides, and in complexes with ligands such as CO, PR_3 , $\eta\text{-C}_5\text{H}_5$. The higher oxidation states VI and VIII are much more readily obtained than for iron, and there is an extensive and important chemistry of the tetraoxides (MO_4), oxohalides, and oxo anions. There are analogies between the chemistries of Ru, Os, and Re, especially in oxo, nitrogen, and nitrido compounds.

For ruthenium, the principal lower oxidation states are 0, II, and III, whereas for osmium they are 0, II, III, and IV. For neither element is the I oxidation state very important.

The oxidation states and stereochemistries are summarized in Table 22-F-1.

The 0 State, d^8 . The chemistry in this state is primarily one of the metal carbonyls; mononuclear and polynuclear carbonyls are known for both elements. Both types undergo substitution reactions, and in the polynuclear species the clusters are often retained. They also undergo protonation reactions, and a variety of hydrido species are known. We do not deal explicitly with these compounds, but some of the chemistry is noted elsewhere (Chapters 25–27, 29, and 30), and certain aspects are described later in this section.

The II State, d^6 . An enormous number of Ru and Os complexes with CO, PR_3 , and similar π -acid ligands are known. For other ligands, the main chemistry is that of chloro, ammonia, and other amine ligands, and again large numbers of complexes exist. The aqua ion $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ has been prepared, but it is readily oxidized to $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$. For osmium the best characterized complexes are those with aromatic amines.

All Ru^{II} and Os^{II} complexes are octahedral and diamagnetic as expected for the t_{2g}^6 configuration. Although these compounds are fairly labile, the reactions often proceed with retention of configuration, suggesting an associative mechanism.

The III State, d^5 . There is an extensive chemistry with both π -acid and σ -donor ligands. Ruthenium(III) species are more common than those of Os^{III} . All the complexes are of low-spin type with one unpaired electron and are octahedral.

The IV State, d^4 . In this state most complexes are neutral or anionic, although a few cationic species such as $[\text{Os}(\text{diars})_2\text{X}_2]^{2+}$ are known; but compared to the II and III states relatively few complexes have been prepared. However it is an important state for Os, where $[\text{OsX}_6]^{2-}$ ions are very stable.

Ru^{IV} and Os^{IV} complexes all have octahedral or distorted octahedral structures, thus should have t_{2g}^4 electron configurations. This configuration is especially subject to anomalous magnetic behavior when the spin-orbit coupling constant of the metal

¹ W. P. Griffith, *The Chemistry of the Rarer Platinum Metals; Os, Ru, Ir and Rh*, Wiley-Interscience, 1967; S. A. Cotton and F. A. Hart, *The Heavy Transition Elements*, Wiley-Halstead, 1975.